

INVESTIGATION OF MERCURY (II) CATALYSED
REACTION BETWEEN POTASSIUM FERROCYANIDE
AND α -NITROSO β -NAPHTHOL : A KINETIC
METHOD FOR TRACE ESTIMATION OF MERCURY (II)

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in Partial Fulfilment of the Requirements
for the Degree of
MASTER OF PHILOSOPHY

By
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to the

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
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STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry under the supervision of Professor P.C. Nigam.

In keeping with general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.


B.R. SRIKANTAMURTHY

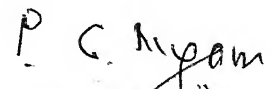
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CERTIFICATE I

This is to certify that Mr. B.R. Srikanta Murthy
has satisfactorily completed all the courses required
for the M.Phil degree programme. These courses include:

Chm 501	Advanced Organic Chemistry
Chm 521	Chemical Binding
Chm 524	Modern Physical Methods in Chemistry
Chm 541	Advanced Inorganic Chemistry I
Chm 542	Advanced Inorganic Chemistry II
Chm 622	Chemical Kinetics
CE 766	Experimental Biochemistry
Chm 800	General Seminar
Chm 801	Graduate Seminar
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CERTIFICATE II

Certified that the work contained in this project report titled, "INVESTIGATION OF MERCURY(II) CATALYSED REACTION BETWEEN POTASSIUM FERROCYANIDE AND α -NITROSO- β -NAPHTHOL : A KINETIC METHOD FOR TRACE ESTIMATION OF Hg(II)," has been carried out by Mr. B.R. Srikanta Murthy under my supervision and the same has not been submitted elsewhere for a degree.

P. C. Nigam

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Kanpur

Nov. 24, 1980.

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B. R. Srikanta Murthy

INVESTIGATION OF MERCURY(II) CATALYSED REACTION
BETWEEN POTASSIUM FERROCYANIDE AND α -NITROSO-
 β -NAPHTHOL : A KINETIC METHOD FOR TRACE ESTI-
MATION OF MERCURY(II)

ABSTRACT

A method is developed for estimation of mercury in catalytic concentration (1×10^{-6} - 1×10^{-5} M) by measuring its catalytic effect on the rate of substitution of cyanide on hexacyanoferrate(II). The progress of reaction was followed spectrophotometrically at 630 nm. The plots of absorbances (after a fixed time of 15, 20 and 25 minutes) vs mercury(II) concentration gave straight lines. The maximum error of the method is $\pm 6.6\%$.

INTRODUCTION

Mercury is one of the highly toxic pollutants present in our environment. It has been reported¹ that many rivers are polluted with mercury which is destroying aquatic life and animal life dependent on the river waters. Chaliyar river in Kerala has a high level of mercury which has infected the river fish making it unsuitable as food. Mercury pollution is assuming dangerous levels in Orissa's Rushkulya river and Thane creek near Bombay where the toxic mercury has found its way in fish, milk and vegetables. River Ganga is reported to contain the highest level of mercury along with other toxic pollutant.

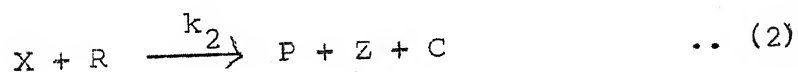
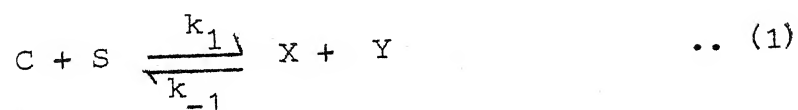
The detection and estimation of mercury is, thus, an important step in the management of any pollution control program relating to this toxic element.

A number of methods such as Atomic Absorption Spectroscopy, Neutron Activation Analysis, Polarography and Nuclear Magnetic Resonance have been available for trace element determination. A recent addition to this list is the kinetic method of analysis which offers some distinct advantages over the conventional methods e.g., simplicity, specificity, accuracy and economy. It is relatively a young area of research and about 45 trace determinations have been reported.²

The catalysis of a reaction due to presence of a trace element or compound can be made use of for determining the concentration of the catalytic species. In the present work a method is developed for the determination of trace concentration of mercury by its effect on the displacement of cyanide in $K_4 Fe(CN)_6$ by nitroso compounds.

GENERAL CATALYST MECHANISM

A reaction involving a catalyst can be represented by the general equations:



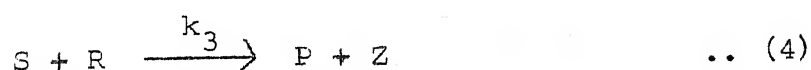
where C represents the catalyst, S is the substrate, X is the intermediate complex formed, Y is a species which may be formed in addition to the complex, R is the reagent which reacts with the complex to give the final product P, with the formation of another molecule Z. The catalyst is regenerated in the reaction. Depending upon stability of the intermediate complex either forward reaction of Equation (1) or Equation (2) may represent the rate determining step.

So either the steady state concentration of X or the equilibrium concentration of X can be used to determine the form of rate expression. For either case it can be shown that

$$\frac{dx(\text{cat})}{dt} = K \alpha_c [C_o] ([R_o] - x) \quad \dots (3)$$

where K is made up of all the rate constants and equilibrium constants, and α_c is the product or a more complex function of all the concentration terms. ($[R_o] - x$ is the reagent concentration at any time t). The value of α_c can be made to remain constant by choosing a large excess of substrate.

If the reaction also proceeds via an uncatalysed path



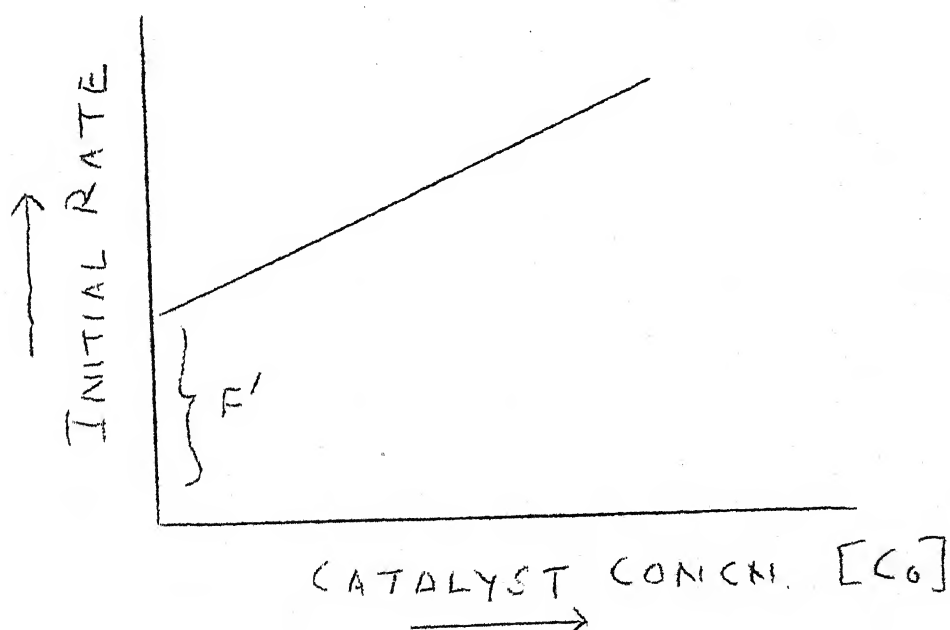
then the total rate of the reaction is given by

$$\begin{aligned} \left[\frac{dx(\text{total})}{dt} \right]_{\text{initial}} &= \frac{dx(\text{cat})}{dt} + \frac{dx(\text{uncat})}{dt} \\ &= K \alpha_c [C_o] ([R_o] - x) + k_3 [S_o] ([R_o] - x) \end{aligned} \quad \dots (5)$$

Dependence of Reaction Rate on Catalyst Concentration

In the beginning of the reaction the extent of reverse reaction and complications resulting from any side reactions are minimal. Therefore, it is advantageous to use the initial rate method. If the small change in concentration of either reactant or product can be measured by a sensitive method then the initial rate of the reaction can be obtained, since the substrate concentration is taken in large excess and x is very small at the start of the reaction $([R]_0 - x) \approx [R]_0$. Equation (5) can be transformed under these conditions to

$$\left[\frac{dx(\text{total})}{dt} \right]_{\text{initial}} = F[C_0] + F' \quad \dots (6)$$



The equation (6) can be represented by the curve in the above figure. The linear relationship between initial

rate and catalyst concentration is clearly established.

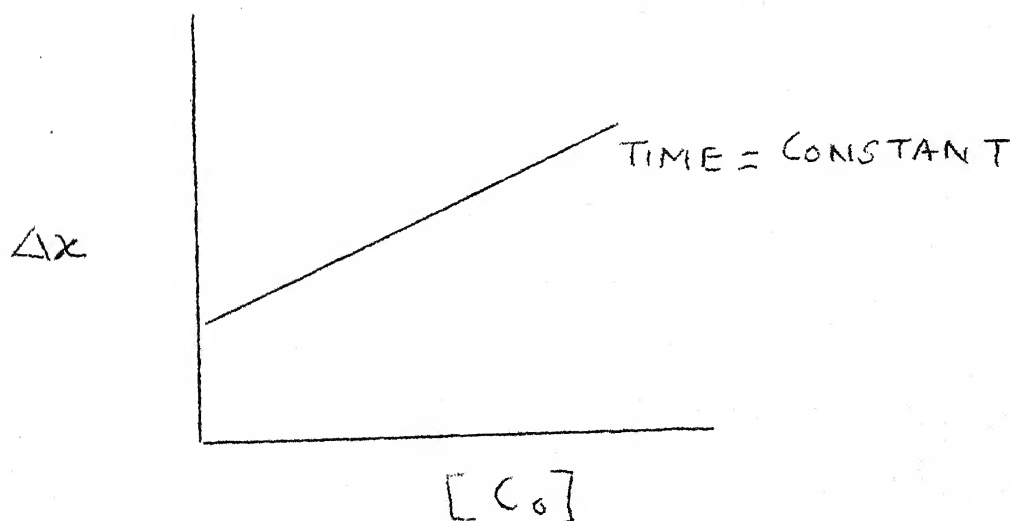
There are two general approaches to estimate the initial rate and hence the concentration of the catalyst:

- (1) Variable time procedure- The time Δt required to produce a fixed change in composition is measured.
- (2) Fixed time procedure- The change in composition Δx produced over a fixed time interval may be measured.

The fixed time procedure has been used to measure the catalyst concentration in this set of experiments for which Equation (6) can be rewritten as

$$\Delta x = (F[C_0] + F')\Delta t \quad \dots (7)$$

Hence a plot of Δx versus $[C_0]$ should give a straight line.



The reaction can be followed spectrophotometrically or by

any physical method and Δx determined at a fixed time after mixing the reagents.

Mercury has been estimated by various workers³⁻⁵ making use of its catalytic effect on the replacement of cyanide in potassium ferrocyanide by various ligands. α -Nitroso- β -naphthol has been selected as a ligand in present study, since it is cheap and commonly available. Its solution in alcohol can be stored for a long time without any observable decomposition.

EXPERIMENTAL

Reagents used:

$K_4 Fe(CN)_6 \cdot 3H_2O$ G.R. (Sarabhai M. Chemicals), α -nitroso- β -naphthol extra pure, abbrev. $\alpha N\beta N$, and $HgCl_2$ A.R. (B.D.H.).

Double distilled water was used to prepare solutions of $K_4 Fe(CN)_6$ and $HgCl_2$. Freshly distilled ethanol was used to prepare solution of $\alpha N\beta N$. 0.1 M $K_4 Fe(CN)_6$ solution was kept in dark amber coloured bottle to prevent its photodecomposition. From this stock solution appropriate dilutions were made just before use. 0.01 M $HgCl_2$ was prepared and stored. The required dilutions were made daily as Hg^{2+} is adsorbed by glass from dilute solutions.

0.01 M α -N β N was prepared in ethanol. From this stock solution appropriate dilutions were made with distilled water just before use.

Equipments used:

Spectronic-20 (Bausch & Lomb), Beckman DB and Cary-17D Spectrophotometers were used for this investigation. Spectronic-20 was used in the visible range. Beckman DB was used in UV and visible range to study the interaction of α -N β N and HgCl_2 . Cary -17D was used for fast scanning experiments. ELICO Digital pH meter model LI-120 was used to adjust the pH of solutions.

SPECTRA OF REACTANTS AND PRODUCTS

The reactants are α -nitroso β -naphthol ($\lambda_{\text{max}} = 263$ nm and 371 nm, $\log \epsilon_1 = 4.1$, $\log \epsilon_2 = 3.6$), $\text{K}_4\text{Fe}(\text{CN})_6$ and HgCl_2 . The first two react together in presence of HgCl_2 to give a green coloured complex ($\lambda_{\text{max}} = 630$ nm). The rate of the reaction is followed by measuring the change in absorbance at 630 nm. At this wave length the absorbances of the reactants are negligible as shown in Fig. 1.

Effect of pH

The following solutions were used to study the effect of pH on the rate of the reaction:

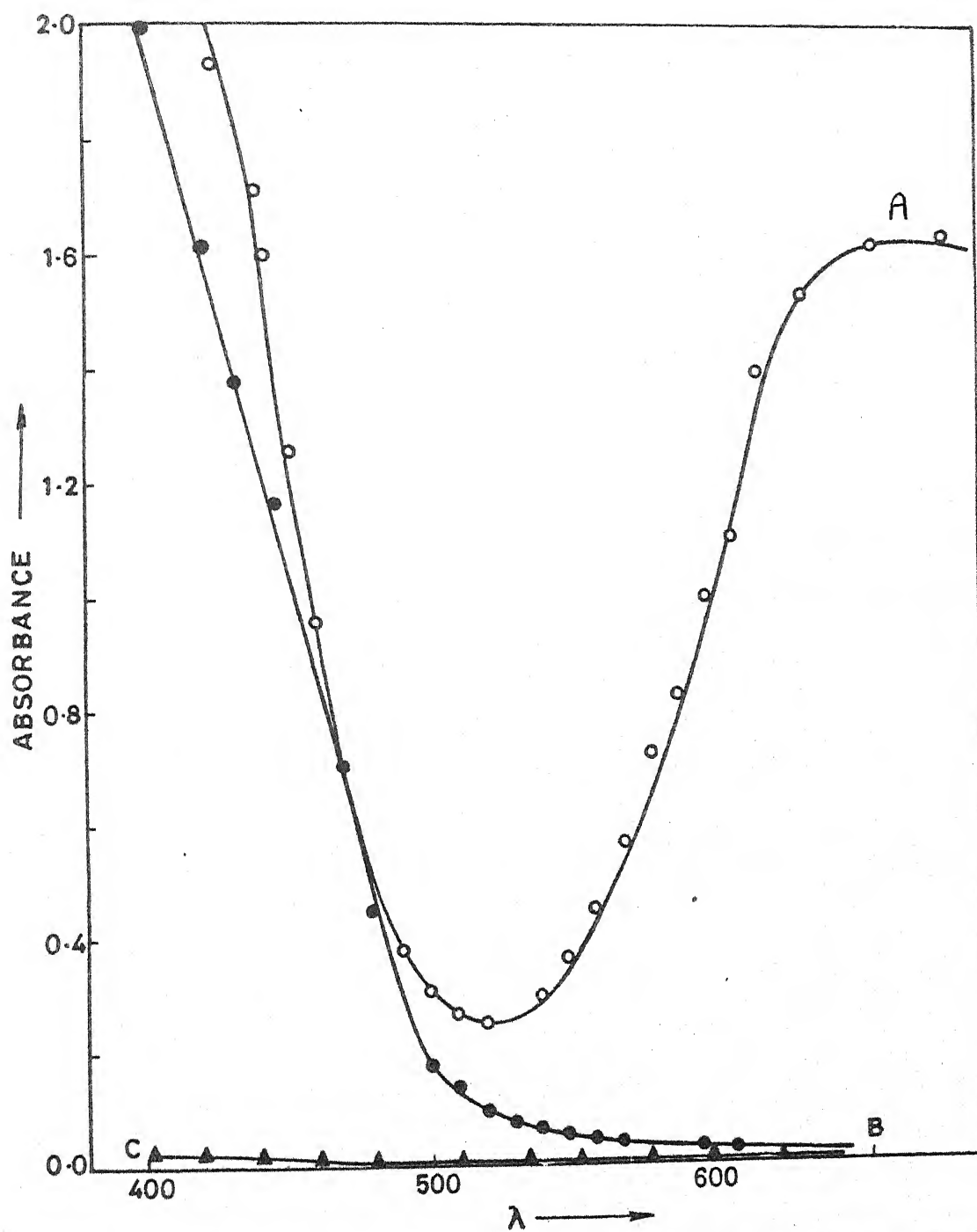


FIG.1. SPECTRA OF REACTANTS AND PRODUCTS IN VISIBLE RANGE.
 A = PRODUCT, B = α -NITROSO β -NAPHTHOL, C = $K_4[Fe(CN)_6]$.

$$[K_4Fe(CN)_6] = 2.5 \times 10^{-3} \text{ M}$$

$$[\alpha N\beta N] = 2.5 \times 10^{-3} \text{ M}$$

$$[HgCl_2] = 5.66 \times 10^{-5} \text{ M}.$$

The rate of the reaction was studied at various pH values at 25°C and 630 nm using fixed time procedure. It was found that the rate of the reaction increases with increase of pH then attains maximum value at pH 2.5 - 3.5 and decreases with further increase of pH. The pH profile of the reaction is given in Fig. 2.

Interaction of $\alpha N\beta N$ and $HgCl_2$

There was some indication that $\alpha N\beta N$ forms a complex with the mercury salt. To study their interaction the following conditions were used:

$$[\alpha N\beta N] = 2 \times 10^{-5} \text{ M}$$

$$[HgCl_2] = 2 \times 10^{-5} \text{ M}$$

$$\text{pH} = 2.5$$

$$\text{Temp.} = 25^\circ\text{C}.$$

5 ml of $\alpha N\beta N$ was mixed with different volumes of $HgCl_2$ and the solutions were made up to 10 ml (Table 1). pH of these solutions were adjusted to 2.5. Spectra of these solutions were recorded in UV as well as in visible regions ($\alpha N\beta N$ has two peaks at 263 nm and 371 nm). It was found that there was no change in absorbance as well as no shift

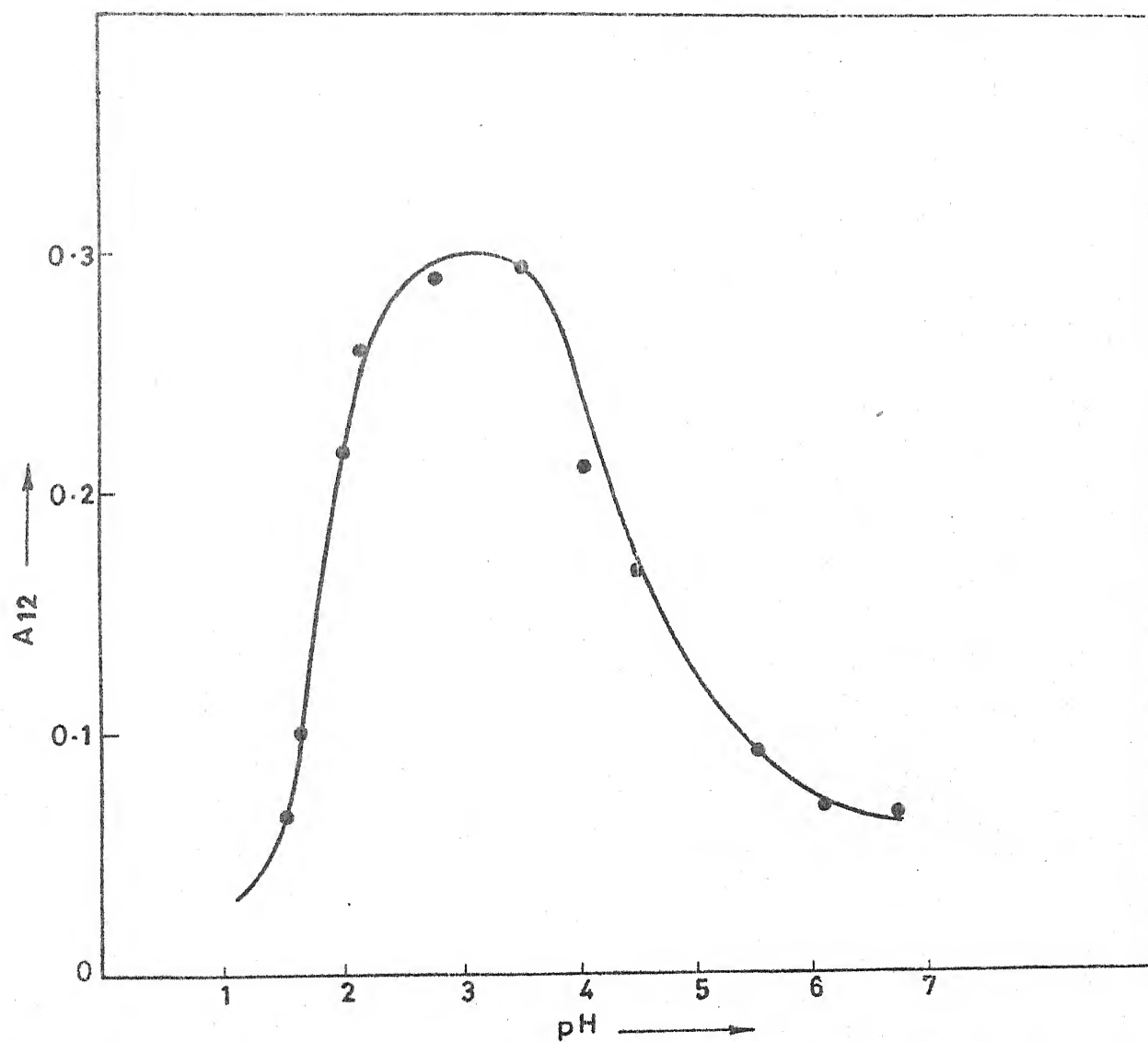


FIG. 2. EFFECT OF pH ON THE RATE OF THE REACTION.

in peak at these two wave lengths. It can be concluded that there is no complex formation between α N β N and HgCl_2 at pH 2.5 (Fig. 3). The concentrations of solution are given in Table 1.

Table 1

Solution Number	Concentration of α -nitroso- β -naphthol	Concentration of mercuric chloride
1	1.0×10^{-5} M	-
2	1.0×10^{-5} M	0.25×10^{-5} M
3	1.0×10^{-5} M	0.50×10^{-5} M
4	1.0×10^{-5} M	0.75×10^{-5} M
5	1.0×10^{-5} M	1.00×10^{-5} M
6	-	1.00×10^{-5} M

The above experiment was repeated at pH 5.6 (Fig. 4). It was found that there was a definite change in absorbance as well a shift in λ_{max} at these two peaks (263 and 371 nm). We can conclude, therefore, that there is complex formation between α N β N and HgCl_2 at pH 5.6. The stoichiometry of this complex was determined by the mole ratio method.

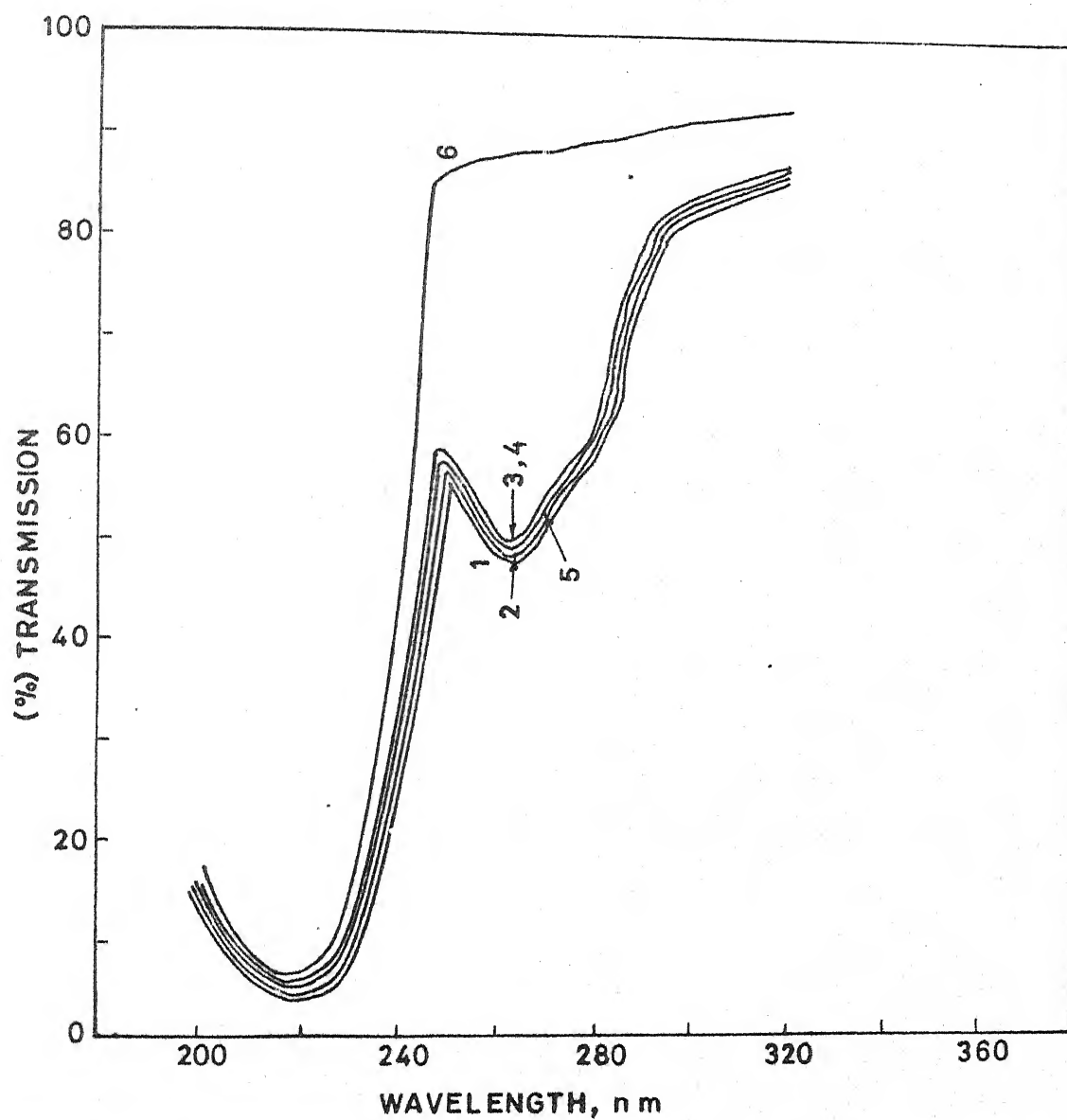


FIG. 3. INTERACTION BETWEEN α -NITROSO β -NAPHTHOL AND HgCl_2 AT pH 2.5.

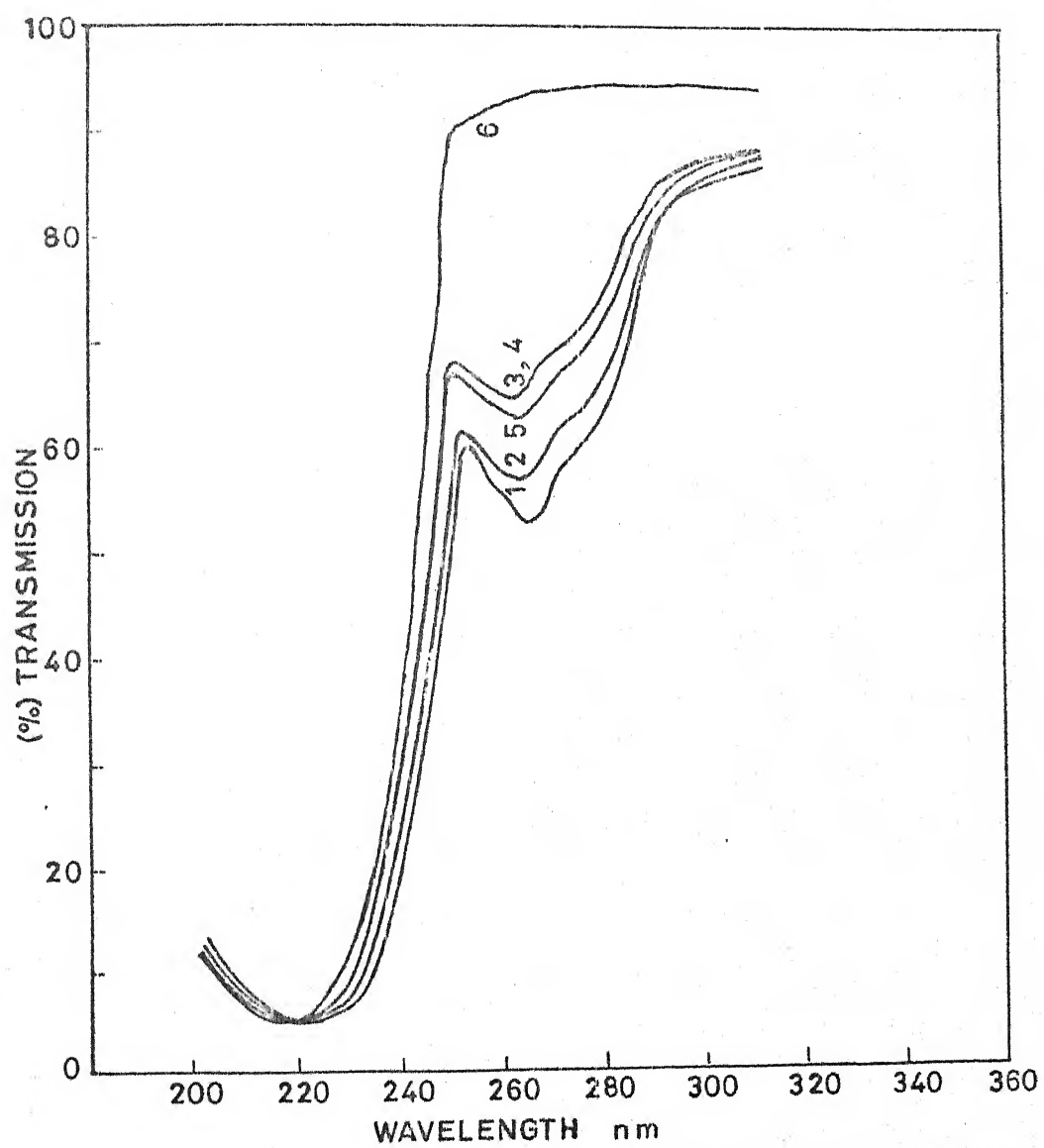


FIG. 4. INTERACTION BETWEEN α -NITROSO β -NAPHTHOL AND HgCl_2 AT pH 5.5.

Mole ratio plot:

To determine the composition of the complex formed between $\chi N\beta N$ and $HgCl_2$ the mole ratio method was employed. The following conditions were used in this experiment:

$$[\chi N\beta N] = 2 \times 10^{-4} \text{ M}$$

$$[HgCl_2] = 2 \times 10^{-4} \text{ M}$$

$$pH = 5.5 - 5.6$$

$$Temp. = 25^\circ C.$$

5 ml of $\chi N\beta N$ was mixed with different volumes of $HgCl_2$ and the solutions made upto 10 ml. pH of each solution was adjusted to 5.5 - 5.6. The absorbance of each solution was measured at 370 nm. From the mole ratio plot (Fig. 5) it was found that metal to ligand ratio in the complex is 1:2.

Following this investigation the Hg^{2+} catalysed reaction of $K_4 Fe(CN)_6$ and $\chi N\beta N$ was carried out at pH 2.5 where the complexation between $\chi N\beta N$ and Hg^{2+} is negligible and mercury acts as a catalyst only.

Absorbance-time curve

The rate of the reaction was monitored by measuring change in absorbance at 530 nm; pH = 2.5 and temperature = $40^\circ C$. Higher temperature was chosen to increase the rate. Theoretically absorbance of the product should gradually increase with time and finally attain a limiting value.

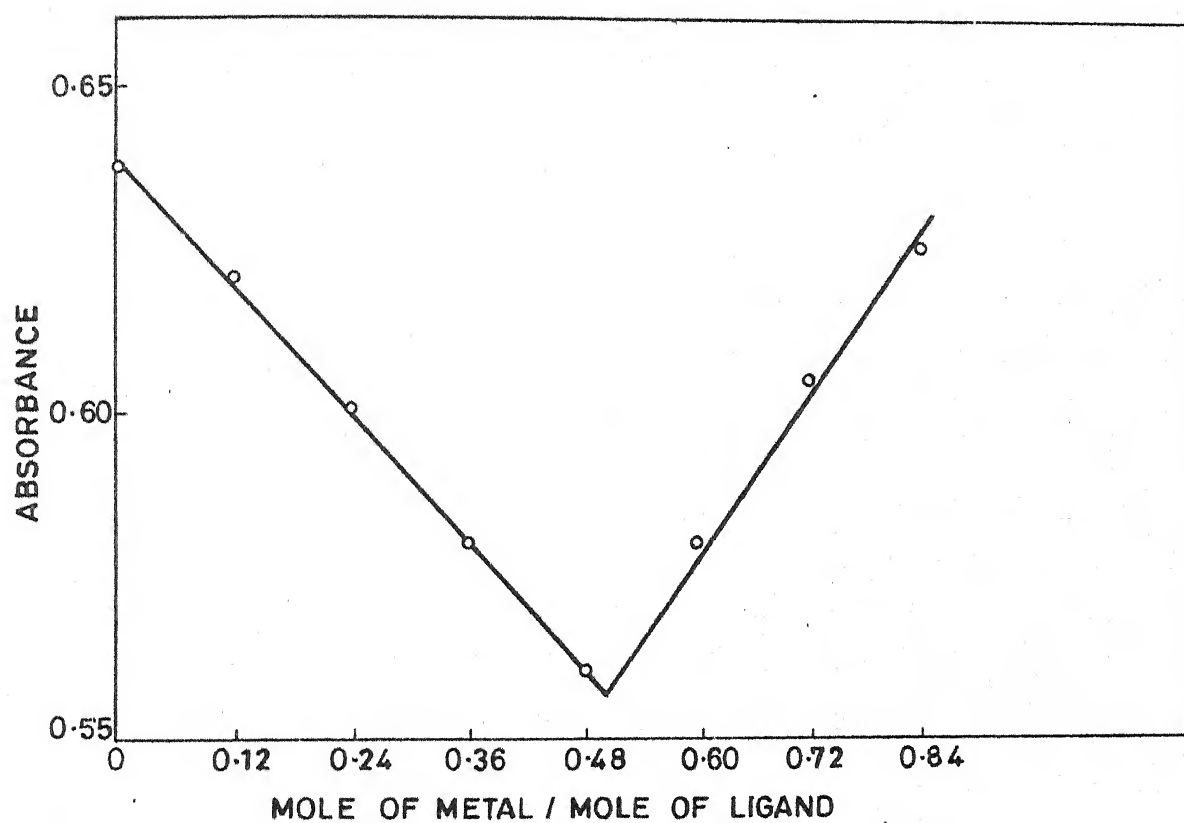
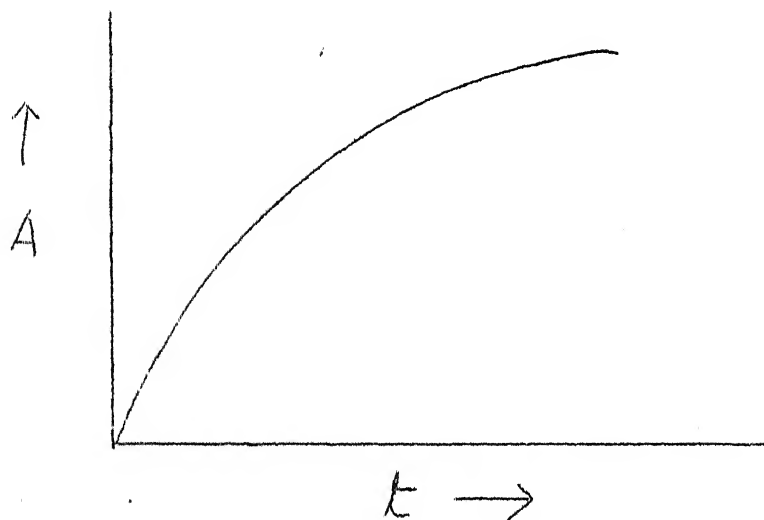


FIG. 5. MOLE RATIO PLOT OF Hg²⁺ AND α-NITROSO β-NAPHTHOL
 $\lambda = 370 \text{ nm}$.

This is represented by the following curve:



In actual experiments the shape of the curve is slightly different as shown in Fig. 6 and Fig. 7. The nature of these curves indicate that there is some induction period for this reaction.

Calibration curves for estimation of mercury

The following conditions were used to obtain the calibration curves: $[\alpha N\beta N] = 1 \times 10^{-2} \text{ M}$, $[K_4Fe(CN)_6] = 10^{-1} \text{ M}$, $[HgCl_2] = 10^{-5} \text{ M} - 10^{-6} \text{ M}$, temp. = $35 \pm 0.1^\circ\text{C}$, pH = 3 ± 0.2 .

1 ml of $\alpha N\beta N$ was mixed with 3 ml of H_2O and the pH adjusted to 2.2 so that pH of the final mixture was 3 ± 0.2 . To this 0.5 ml of $K_4Fe(CN)_6$ and 0.5 ml of $HgCl_2$ of chosen concentrations were added. Absorbance of each solution was measured at 630 nm for about 1 hour. From such curves absorbances at 15, 20, 25 minutes were read off (Table 2) and

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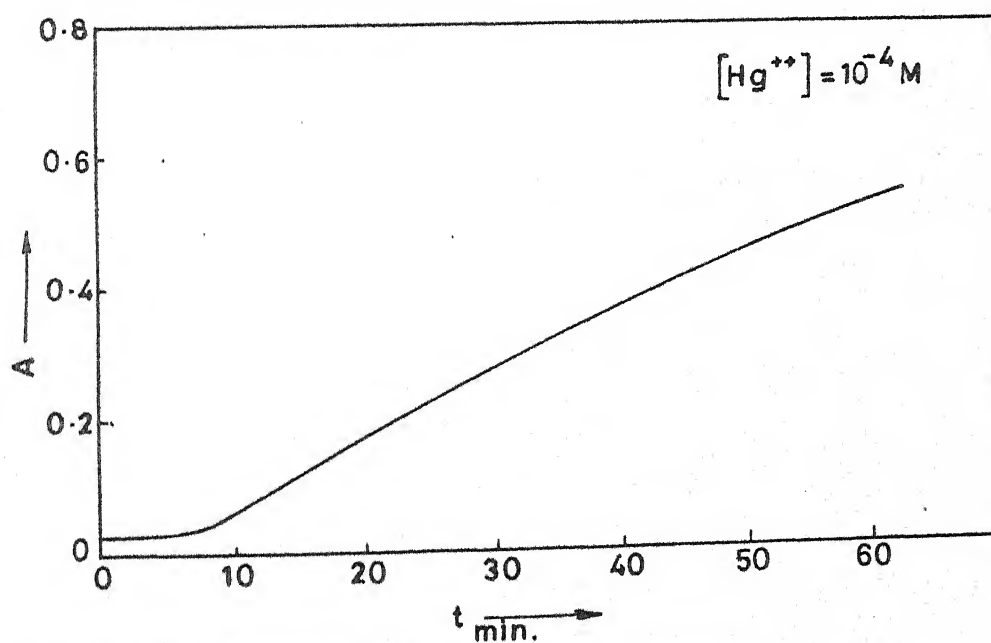
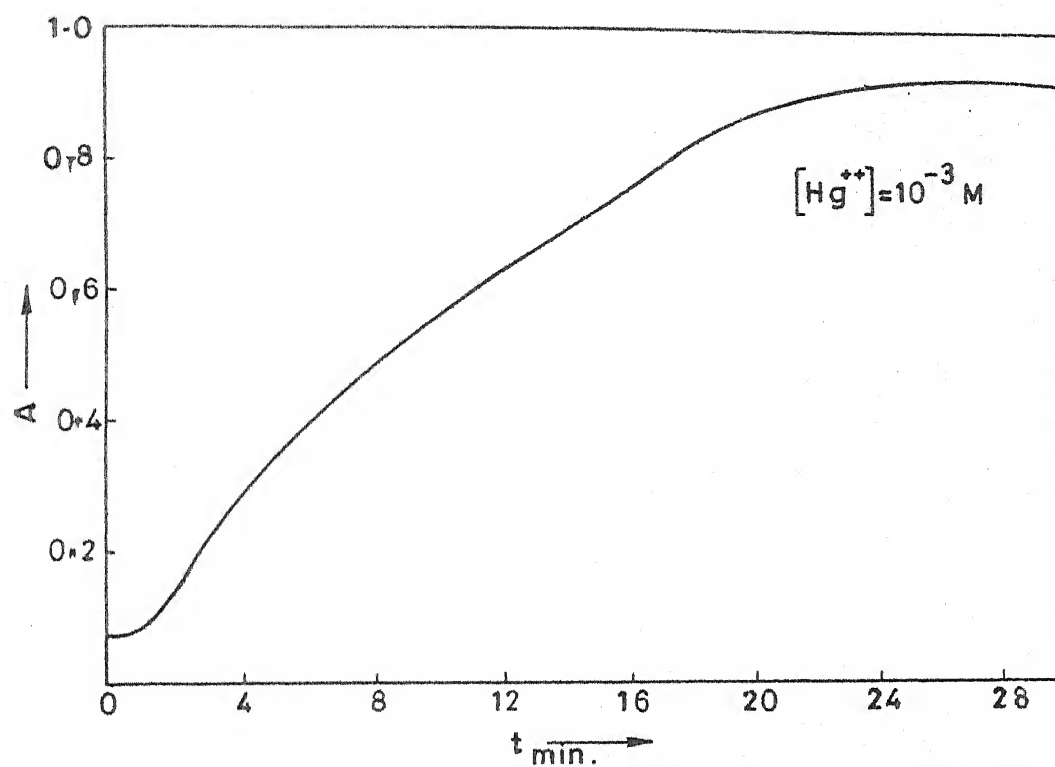


FIG. 6 - 7 ABSORBANCE DURING A KINETIC RUN.
 $[d. N. B. N.] = 10^{-3} M$, $[K_4 Fe(CN)_6] = 10^{-3} M$, TEMP. = $35^\circ C$

Table 2

Absorbance at Fixed Time for Various $[\text{Hg}^{2+}]$

$[\text{Fe}(\text{CN})_6^{4-}] = 1.0 \times 10^{-2} \text{ M}; \text{ } \cancel{N} \text{ } N = 2 \times 10^{-3} \text{ M},$

$\text{pH} = 3 \pm 0.2, t = 35 \pm 0.1^\circ\text{C}, \mu = 0.1 \text{ M}$

Concentration of $[\text{Hg}] \times 10^6$	A_{15}	A_{20}	A_{25}
1.0	0.148	0.182	0.193
2.0	0.177	0.222	0.245
3.0	0.220	0.273	0.310
4.0	0.252	0.312	0.360
5.0	0.285	0.352	0.412
6.0	0.332	0.405	0.475
7.0	0.362	0.445	0.525
8.0	0.395	0.485	0.580
9.0	0.435	0.530	0.640
10.0	0.465	0.570	0.700

From Least square fits the following relationships are obtained:

$$A_{15} = 0.3586 \times 10^5 [\text{Hg}^{2+}] + 0.110 \quad \dots (8)$$

$$A_{20} = 0.4356 \times 10^5 [\text{Hg}^{2+}] + 0.138 \quad \dots (9)$$

$$A_{25} = 0.5617 \times 10^5 [\text{Hg}^{2+}] + 0.135 \quad \dots (10)$$

The maximum error of the method is $\pm 6.6\%$.

plotted against mercury concentration. These plots are found to be linear as shown in Fig. 8. The points shown on the curves are average of absorbance values of at least three kinetic runs.

The percentage error for each run was calculated and has been given in Table 3.

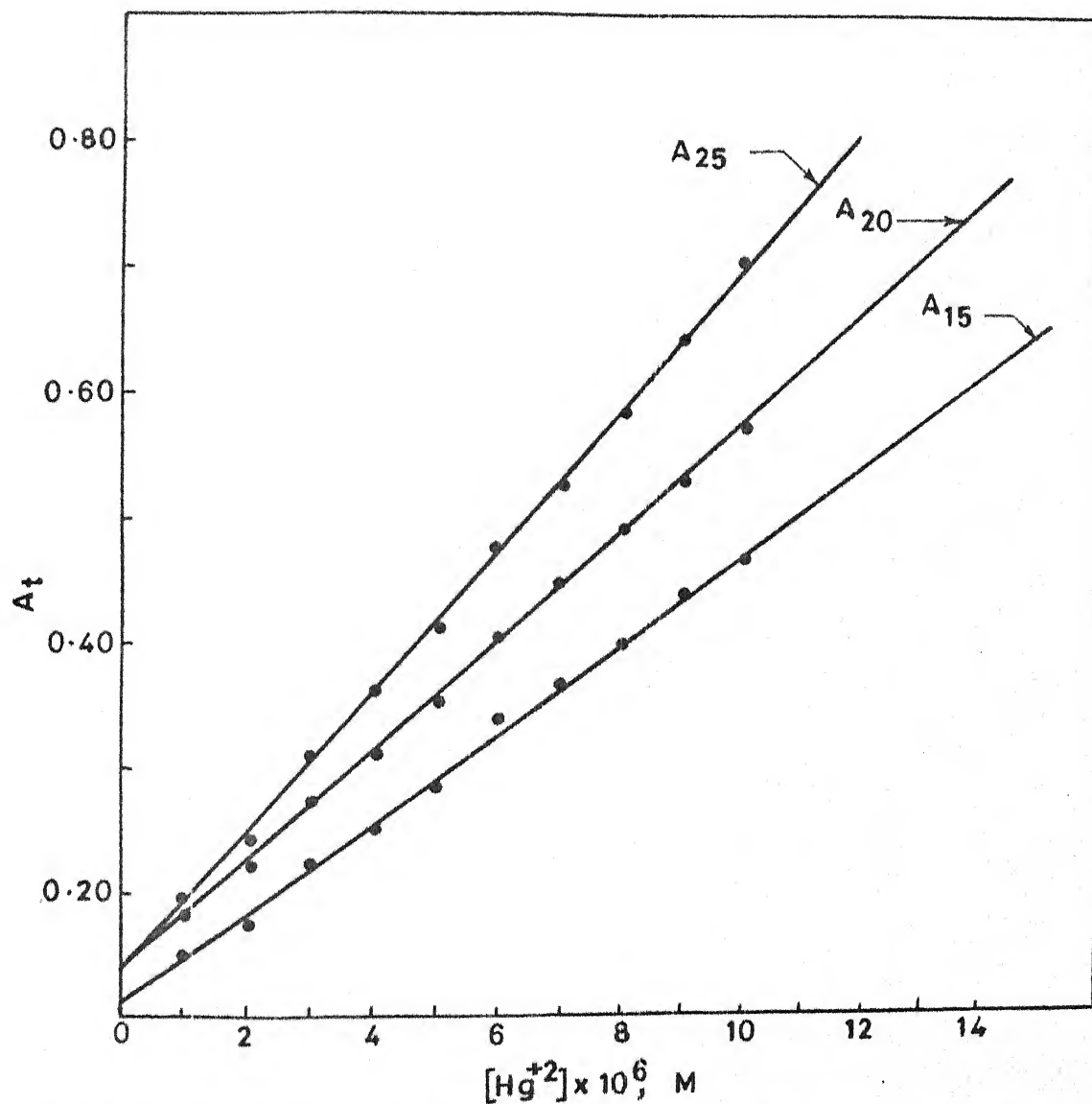


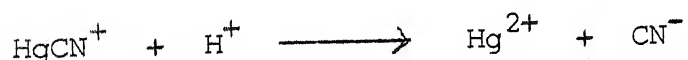
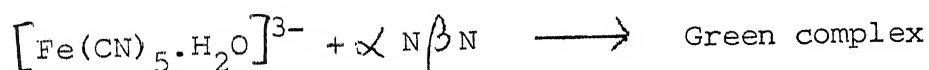
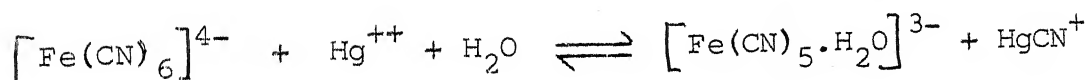
FIG. 8 ABSORBANCE AT FIXED TIME VS. Hg^{2+} CONCENTRATION
 $[\text{d. N. B. N.}] = 2 \times 10^{-3} \text{ M}$, $[\text{K}_4 \text{Fe}(\text{CN})_6] = 1.0 \times 10^{-2} \text{ M}$, TEMP. = 35° C

Table 3

$[\text{Hg}^{2+}] \times 10^6$ Taken	A_{15}			A_{20}			A_{25}		
	$[\text{Hg}^{2+}] \times 10^6$ Found	% Error		$[\text{Hg}^{2+}] \times 10^6$ Found	% Error		$[\text{Hg}^{2+}] \times 10^6$ Found	% Error	
1.0	1.059	5.90		1.010	1.01		1.050	5.00	
2.0	1.860	-6.58		1.928	-3.58		1.958	-2.08	
3.0	3.067	2.23		3.090	3.30		3.079	2.60	
4.0	3.960	-1.00		3.994	-0.14		4.005	0.12	
5.0	4.880	-2.39		4.910	-1.74		4.930	-1.37	
6.0	6.270	4.50		6.120	2.12		6.050	0.88	
7.0	7.027	0.39		7.047	0.68		6.980	-0.81	
8.0	7.940	-0.65		7.966	-0.42		7.940	-0.65	
9.0	9.060	0.66		8.999	-0.19		8.990	-0.10	
10.0	9.899	-1.06		9.917	-0.82		10.050	0.58	

DISCUSSION

The probable mechanism of the reaction and role of the mercury catalyst in the reaction can be understood if the reaction is assumed to take place according to the following scheme:



Earlier work⁶⁻⁹ supports this hypothesis. The role of mercury is to extract the CN^- from hexacyanoferrate ion enabling the solvent molecule, in this case water, to replace the same. The pentacyanoaquoferate reacts with $\alpha \text{N} \beta \text{N}$ according to step (2). Hg^{2+} is regenerated in the third step and can be reused in a cyclic manner.

The effect of pH on the rate of reaction (Fig. 2) can be rationalised on the basis of the above proposed scheme. At high pH regeneration of mercury is not possible according to step 3. High pH also results in precipitation of the hydroxide of mercury. Added to this is the tendency of $\alpha \text{N} \beta \text{N}$ to complex with mercury at higher pH to form a 1:2 complex (Fig. 5). As the pH is lowered the rate increases

understandably. The rate again decreases at $\text{pH} < 2.2$ which is probably due to the formation of more stable and kinetically less reactive protonated forms of hexacyanoferrate viz., $[\text{HFe}(\text{CN})_6]^{3-}$, $[\text{H}_2\text{Fe}(\text{CN})_6]^{2-}$, $[\text{H}_3(\text{FeCN})_6]^{-1}$ etc.⁷

A time scan of the reaction mixture between 350 - 800 nm (Fig. 9) shows that the absorbance increases at λ_{max} (630 nm) of the complex as well as λ_{max} (370 nm) of $\alpha\text{N}\beta\text{N}$. This can happen if the complex between $[\text{Fe}(\text{CN})_6]^{4-}$ and $\alpha\text{N}\beta\text{N}$ also absorbs close to 370 nm and its extinction coefficient is relatively high. In that case the decreasing peak of $\alpha\text{N}\beta\text{N}$ will be buried under the increasing peak of the complex as the reaction proceeds. A second time scan has been taken (Fig. 10) between 400-800 nm to clearly depict the increase in concentration to the complex with progress of reaction as shown by continual increase in absorbance at 630 nm.

The analytical application of this reaction is promising because it enables one to determine the concentration of mercury in trace amounts (10^{-5} - 10^{-6} M). Though interferences have not been investigated in detail, it is found that metals forming complexes with cyanide ion e.g., Au, Ag, Cd, etc. will interfere to some extent.

Qualitatively it has been verified that many common metal ions other than the ones mentioned above do not interfere in this analysis. The concentration of Hg^{2+} can be calculated from equations 8, 9 and 10. The maximum error of the

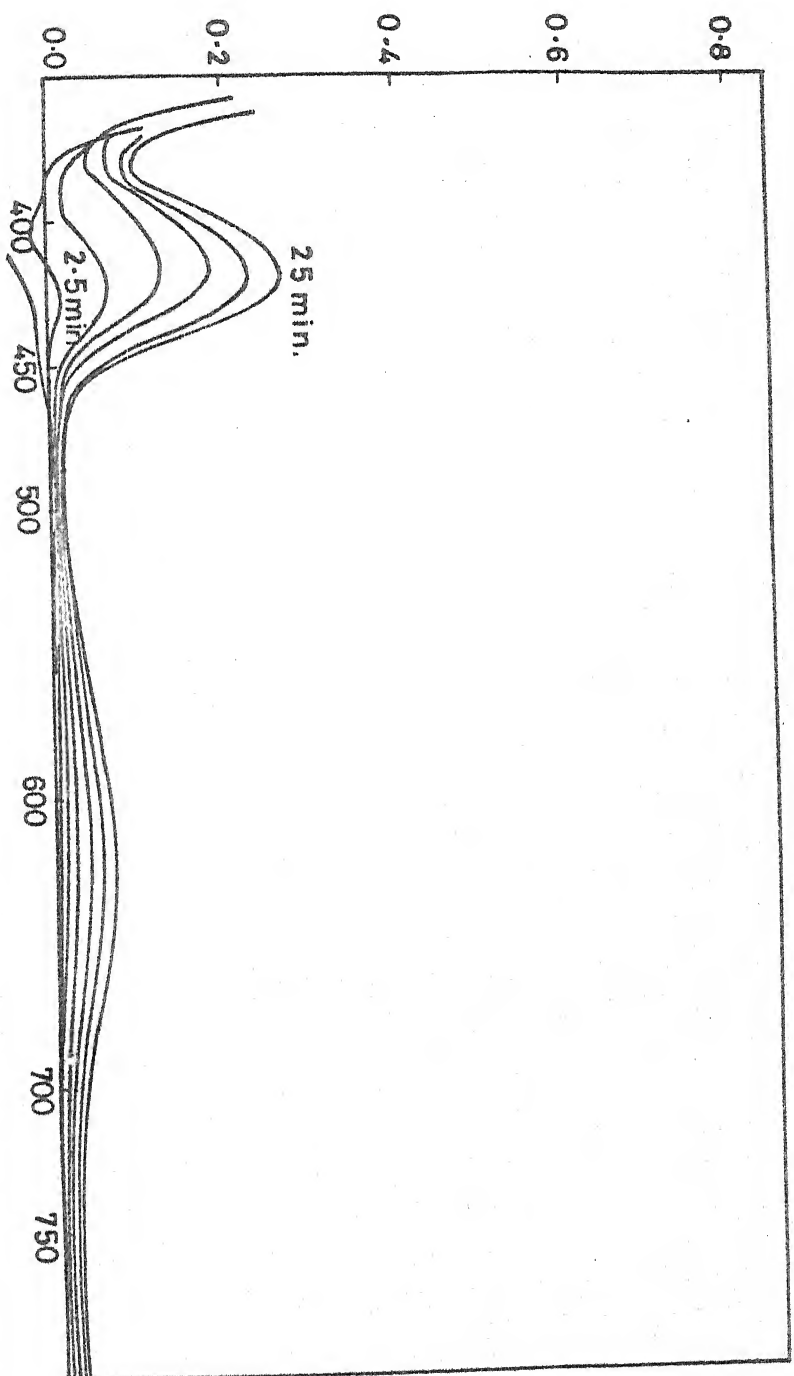


FIG. 9. RAPID SCAN OF REACTION MIXTURE DURING A KINETIC RUN BETWEEN 400-800 nm. $[\alpha. N. \beta. N] = 1 \times 10^{-3} M$, $[K_4 Fe(CN)_6] = 0.5 \times 10^{-1} M$, $[HgCl_2] = 2.5 \times 10^{-4} M$.
REFERENCE = $\alpha. N. \beta. N$.

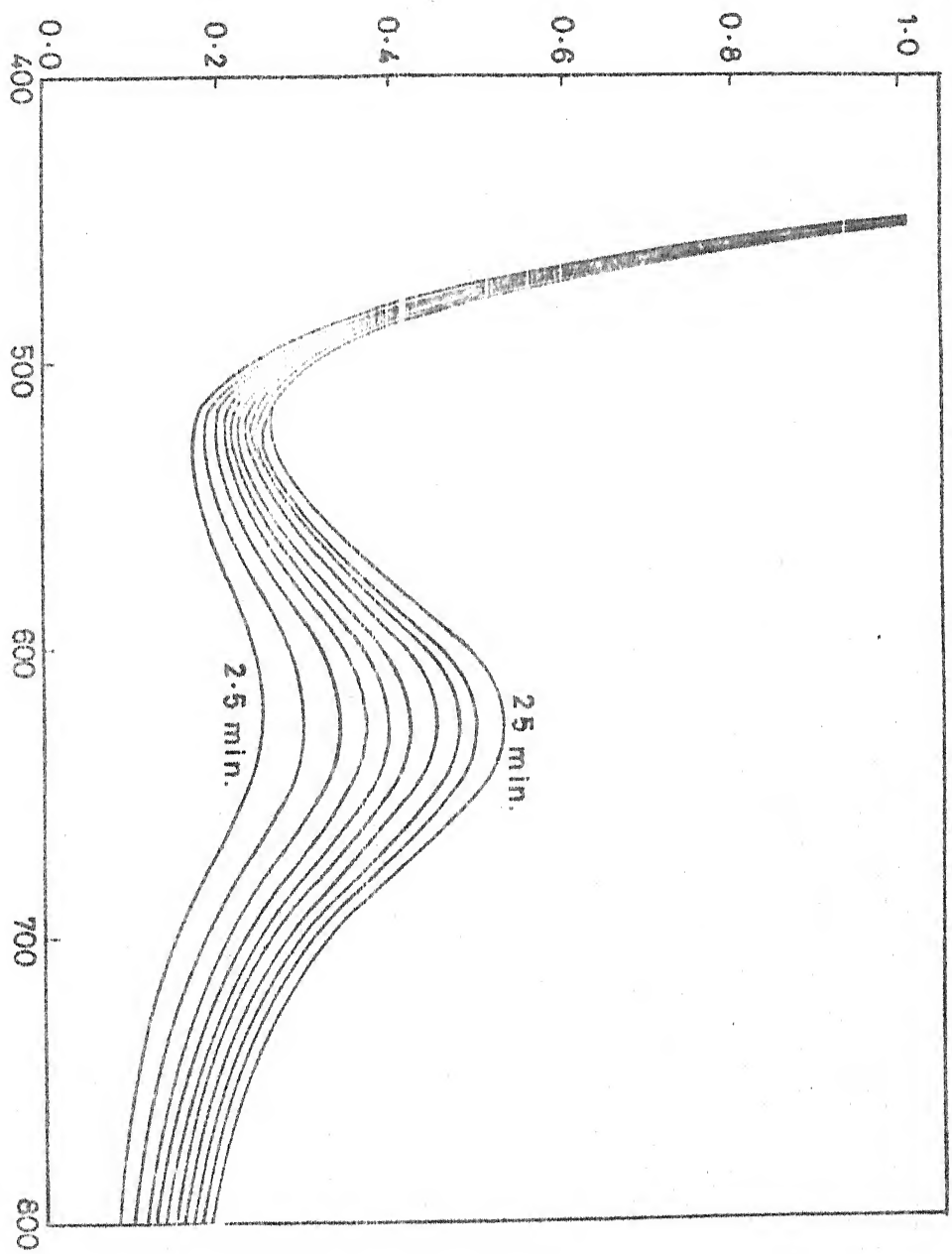


FIG. 10 RAPID SCAN OF REACTION MIXTURE BETWEEN 400-800 nm
 $[\alpha. N. B. N] = 1 \times 10^{-3} M$, $[K_4 Fe(CN)_6] = 0.5 \times 10^{-1} M$, $[HgCl_2] = 2.5 \times 10^{-3} M$.
 REFERENCE = DISTILLED WATER. ↓

method has been found to be $\pm 6.6\%$ (Table 3) which is acceptable at this small concentration of mercury present in solution. The lowest detection limit is 10^{-6} M.

At the risk of repetition it has been demonstrated that the mercury(II) catalysed reaction between hexacyanoferrate(II) and α -N β -N can be used to estimate the concentration of mercury under specified conditions down to the concentration range of 10^{-6} M. The method is simple, cheap and dependable.

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